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25 YEAR RE-REVIEW

Synthesis and transformations of trialkylsilylethynylvinylalkyl ethers.

M. F. Shostakovskiy, E. P. Gracheva and L. A. Kayutenko (N.D.Zelinskii Inst. Org. Chem., Moscow). Doklady Akad. Nauk S.S.S.R. 132, 153-6 (1960).

falm

man

Passage of diacetylene into 2% alc. KOH under N_2 at 70-5° gave ethynylvinyl butyl ether, b_{12} 61.5°, n_D^{20} 1.4712, d_{20} 0.8664. This added to EtMgBr, stirred 4-5 hrs. and treated with Me_3SiCl gave after ~~xxxxxx~~ standing overnight and stirring 3 hrs. 50.7% $Me_3SiC{:}CCH{:}CHOEt$ (I), b_{15} 110-2°, 1.4695, 0.8589. Similarly was prepd. 52.3% $Et_3SiC{:}CCH{:}CHOEt$, b_7 105-6°, 1.4895, 0.8886. The former with aq. H_2SO_4 and $NaHSO_3$ was 79% hydrolyzed in 30 min. At 50°, the reaction is complete in 1 hr., yielding tetrolaldehyde. Hydrogenation of I over $Pd\text{-}CaCO_3$ gave ~~xxxxxxxx~~ $Me_3SiCH{:}CHCH{:}CHOEt$, b_7 88-90°, 1.4580, 0.8532. I and maleic anhydride in C_6H_6 gave in 1 hr. refluxing 25.7% phthalic anhydride.

Reaction of alkylcyclosiloxanes with titanium tetrachloride.

K. A. Andrianov and A. I. Petrashko (Inst. Hetero-org. Compds., Moscow).

Doklady Akad. Nauk S.S.S.R. 131, 561-2 (1959).

Heating 80 g. $(Me_2SiO)_4$ and 52 g. $TiCl_4$ 6 hrs. at 170° gave 27 g. $Cl(Me_2$-$SiO)_4TiCl_3$, b_2 97-8°. Similarly was prepd. $Cl(Et_2SiO)_3TiCl_3$, b_2 141-3°. Formation of such compds. is believed to occur through initial formation of a coordination complex between the Ti atom and one O atom of the siloxane ring, after which the latter is opened to yield the above products.

Intermediates for synthetic clays - interesting materials - high temperature application.

Organo silicon + titanium

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Methylalkoxychlorosilanes. Reactive organo silicon compounds

K. A. Andrianov and A. A. Kazakova (All Union Electrotech. Inst., Moscow).

Zhur. Obshchei Khim. 29, 3754-7 (1959).

Addn. of ROH with $MeSiCl_3$, stirring 1 hr., followed by 5-12 hrs. at 50-60° gave: 43% $MeSiCl_2OMe$, b_{760} 79-80°, d^{20}_{20} 1.1424, n^{20}_D 1.3945; 38% $MeSiCl(OMe)_2$, b_{760} 93-4°, 1.0426, 1.3820; 27% $MeSiCl_2(OEt)$, b_{760} 98-101°, 1.1037, 1.3990; 23% $MeSiCl(OEt)_2$, b_{760} 127-31°, 0.9822, 1.3912; 35% $MeSiCl_2OBu$, b_{760} 144-6°, 1.0486, 1.4138; 43% $MeSiCl(OBu)_2$, b_{760} 202-4°, 0.9398, 1.4130; 25% $MeSiCl_2$-$OCH_2CH_2CHMe_2$, b_{16} 56-7°, 1.0341, 1.4158; $(iso\text{-}AmO)_2SiMeCl$, b_{20} 105°, 0.9283, 1.4172. These were hydrolyzed in $MePh\text{-}H_2O$ mixt. at 20-5°, with insol. polysiloxanes being obtained from all monomers except $MeSiCl(OBu)_2$ and $(iso\text{-}AmO)_2MeSiCl$, which gave sol. products.

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Infrared absorption spectra of poly-(alumino-organosiloxanes) and poly-(titano-organosiloxanes).

K. A. Andrianov, N. P. Gashnikova and E. Z. Asnovich (Inst. Hetero-org. Compds Moscow). Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk 1960, 857-62.

Infrared absorption spectra are shown for specimens of poly-(aluminomethylsiloxane), poly-(aluminumethylsiloxane), poly-(aluminumphenylsiloxane), poly-(titanium-methylsiloxane), poly-(titaniumethylsiloxane), poly-(titaniumphenylsiloxane), as well as polymethylsiloxane, polyethylsiloxane and polyphenylsiloxane. The characteristics bands of Al-O vibration in the Al-O-Si grouping are at 1080-1050 cm^{-1}; those for Ti-O bond in Ti-O-Si grouping lie at 914-22 cm^{-1}. The polymers appear to be consitituted in the form of chains of cyclic structures, in which predominantly tetrameric siloxane and metallosiloxane rings are bound to each other through O links.

organosilicon

 he presence of iron pentacarbonyl and nickel chloride. Korea(?)

R. Kh. Freidlina, Tsao I and E. Ts. Chukovskaya (Inst. Hetero-org. Compds., Moscow). Doklady Akad. Nauk S.S.S.R. 132, 149-52 (1960).

Heating 115 g. $MeSiHCl_2$, 160 g. CH_2:CHCN, and 1.0 ml. $Fe(CO)_5$ 0.15 g. $NiCl_2$ in stainless steel autoclave under N_2 (30 atm. initially) 5 hrs. at 120-30° gave 60% $MeSiCl_2CHMeCN$, b_1 59-60°, n_D^{20} 1.4490, d_{20} 1.1635. The isomeric product was totally absent, as shown by Raman spectrum and chem. tests. Treated with MeMgBr it gave $Me_3SiCHMeCN$, 70%, b_{20} 71.5°, 1.4245, 0.8303; excess RMgX gave also some MeCOEt. Hydrolysis of the nitrile gave $(Me_3Si)_2O$ and $EtCO_2H$. Reaction of 87 g. Et_3SiH, 132 g. CH_2:CHCN, 0.5 ml. $Fe(CO)_5$ and 0.2 g. $NiCl_2$ similarly gave 73% $EtSiCl_2CHMeCN$, b_8 97-8°, 1.4525, 0.8634. Without the added catalysts, the reaction fails; $NiCl_2$ alone is also ineffective; $Fe(CO)_5$ alone is also ineffective in a steel autoclave, but the 2 catalysts do effect the reaction either in a sealed ampul or in autoclave in which case the Fe component is formed on the vessel walls.

 s by reaction of hydrosilanes with olefins in the presence of iron pentacarbonyl.

R. Kh. Freidlina, E. Ts. Chukovskaya, Tsao I and A. N. Nesmeyanov (Inst. Hetero-org. Compds, Moscow). Doklady Akad. Nauk S.S.S.R. 132, 374-7 (1960) cf. 127, 352 (1959). Karsa(?)

Heating 34 g. Et_3SiH and 0.5 ml. $Fe(CO)_5$ under N_2 and 45 atm. C_2H_4 in a steel autoclave 5 hrs. at 130° gave 66% $Et_3SiCH{:}CH_2$, b. 144.5°, n_D^{20} 1.4330, d_{20} 0.7718; with 5 atm. C_2H_4 initially, there formed 73% Et_4Si. Similarly 63 g. 1-decene, 70 g. $MeSiHCl_2$ and 0.2 ml. $Fe(CO)_2$ in 5 hrs. at 140° gave some decane, and mixed $C_{10}H_{21}SiMeCl_2$-$MeSiCl_2C_{10}H_{19}$, b_3 122°. Treatment with MeMgBr gave $C_{13}SiH_{28-30}$ b_1 85-6°, 1.4390, 0.7797. Examn. of the infra red spectrum showed the presence of both $Me_3SiCH{:}CHC_8H_{17}$ and $Me_3SiCH_2CH{:}CH$-C_7H_{15}. Treatment with H_2SO_4 gave $(Me_3Si)_2O$. $MeSiHCl_2$, C_3H_6 and $Fe(CO)_5$ similarly gave a product $C_4H_{8-10}SiCl_2$, b. 124-30°, 1.4380, 1.0553, which methylated to $C_6H_{14-16}Si$, b. 87-8°, 1.4042, 0.7147, containing Me_3Si-$CH{:}CHMe$ and Me_3SiCH_2Et; treatment with H_2SO_4 gave 25% satd. material, ~~ex~~ Me_3SiPr and $(Me_3Si)_2O$. $Et_3SiCH{:}CHOEt$ gives a gradually rising thiocyanate or bromine number, the rise being attributed to side reactions; treatment with acidic soln. of 2,4-dinitrophenylhydrazine gave AcH 2,4-dinitrophenylhydrazone; the original ethoxy deriv. has infra red bands at 1597 and 1609 cm^{-1} typical of vinyl ethers.

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Radical addition reactions to α-, β- and γ-alkenylsilanes.

E. A. Chernyshev (N.D.Zelinskii Inst. Org. Chem., Moscow). Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk 1960, 80-3.

cf. 1956, 1445.

Vinyl- and γ-butenylsilanes readily undergo radical addn. reactions while allylsilanes do so poorly. This confirms the conjugation of the double bond in β-position relative to Si. Addn. of 1.5 g. Bz_2O_2 in 49 g. PrCHO to boiling mixt. of 30 g. $MeEt_2SiCH_2CH_2CH{:}CH_2$ and 49 g. PrCHO over 2 hrs. and heating 50 hrs. longer ~~gxxm~~ (4.5 g. Bz_2O_2 added gradually) gave after an aq. treatment 12.2 g. 3-methyl-3-ethyl-3-sila-8-undecanone, $b_{3.5}$ 127-8°, n_D^{20} 1.4470, d_{20} 0.8605; 2,4-dinitrophenylhydrazone, m. 134°. Similarly BzH gave 32% 3-methyl-3-ethyl-3-sila-8-phenyl-8-octanone, $b_{3.5}$ 163-4°, 1.5168, 0.9726. Similarly $CHCl_3$ in 50 hrs. gave 72% 1,1,1-trichloro-6-methyl-6-ethyl-6-silaoctane, b_3 127-9°, 1.4647, 1.0578. With CCl_4 there was formed 78% 1,1,1,3-tetrachloro-6-methyl-6-ethyl-6-silaoctane, $b_{3.5}$ 128-30°, 1.4860, 1.1684.

[redacted]

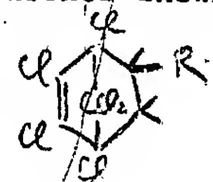
organosilicon

Synthesis of organosilicon monomers from hexachlorocyclopentadiene and 5,5-difluorotetrachlorocyclopentadiene.

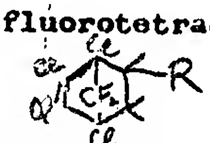
V. A. Ponomarenko and A. D. Snegova (N.D.Zelinskii Inst. Org. Chem., Moscow).

Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk 1960, 135-8.

Refluxing hexachlorocyclopentadiene with various vinyl or allyl derivs. of Si gave 41-72% yields of adducts which are listed below as A (substitutents shown):

A 

$SiCl_3$, b_2 138°, n_D^{20} 1.5573, d_{20} 1.7362; $MeSiCl_2$, b_2 136-7°, 1.5530, 1.6457; $EtSiCl_2$, b_7 160°, 1.5520, 1.6065; CH_2SiHCl_2, b_6 152°, 1.5500, 1.6370. Similarly 5,5-difluorotetrachlorocyclopentadiene gave B:

B 

$SiCl_3$, b_{10} 130°, 1.5141, 1.7010; $MeSiCl_2$, b_8 130°, 1.5120, 1.6041; $SiHCl_2$, b_{16} 88°, 1.4326, 1.4474; CH_2SiHCl_2, $b_{2.5}$ 102-3°, 1.5110, 1.5982; SiHMeCl, b_8 122°, 1.5066, 1.5355. CH_2:CHClSiCl_3, ClCH:CHSiCl_3 and EtSiCl_2CF:CF_2 failed to react. The group refraction of the cyclic portion of A+Si is shown to display about 1 unit neg. exaltation; for B+Si this is also about 1 neg. unit.

(1) Mechanism of the reaction of addition of organo silicon hydrides to unsaturated compounds in the presence of platinized carbon and chloroplatinic acid. V. A. Ponomarenko, G. V. Odabashyan and A. D. Petrov (N.D.Zelinskii Inst. Org. Chem., Moscow). Doklady Akad. Nauk S.S.S.R. 131, 321-4 (1959). The Pt catalyst greatly facilitates the cleavage of the Si%h bonds in Si hydrides, such as $MeEt_2SiH$, Et_3SiH, $PhSiH_3$, Ph_2SiH_2, Ph_3SiH, and CH_2:CH-CH_2OCF_2CHFCl, as shown by hydrogenation of diphenylpicrylhydrazyl radical added to such systems at 94^o. Thus the Pt catalyst yields atomic H which is attacked by the free radical hydrazyl. The homolytic cleavage of the SiH bond is decreased by steric factors, so that Ph_3SiH is practically unreactive. The following descending reactivity scale is found: Et_2MeSiH, MeEtSiHCl, $EtSiHCl_2$ and $HSiCl_3$. The homolytic process evidently starts on the surface of the C in the Pt-C catalyst. The conclusion is also confirmed by H-D exchange which occurs between $EtSiHCl_2$ and $MeEt_2SiD$ only in the presence of Pt-C catalyst at 150-68^o in 2 hrs. These results suggested the use of dimethylcyanamide as a suitable catalyst for addn. of Si hydrides to unsatd. compds. This was verified exptly. Heating 40.6 g. $HSiCl_3$ and 15.5 g. CH_2:CHCN with 3 g. dimethylcyanamide 2 hrs. to 124-68^o (exothermic) gave 37% $Cl_3SiCH_2CH_2CN$, b_{15} 92-4^o, m. 34-5^o. Heating $Et_2MeSiCl$ with LiH in Bu_2O 20 hrs. in autoclave gave 50% $MeEt_2SiD$, b_{735} 76.8^o, d_{20} 0.7102, n_D^{20} 1.3975. Thus the addn. of Si hydrides to olefins is primarily a homolytic process.

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Organoboron & exotic fuels

Synthesis and some transformations of alkylmercaptodiboranes.

B. M. Mikhailov and T. A. Shchegoleva (N.D. Zelinskii Inst. Org. Chem., Moscow). Doklady Akad. Nauk S.S.S.R. 131, 843-6 (1960). cf. Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk 1959, 1868.

All the reactions below were run under N. Passage of 0.055 mole B_2H_6 into 40.5 g. BuSH in Et_2O at room temp. and allowing the mixt. to stand overnight gave 75% $[HB(SBu)_2]_2$, b_2 98-103°, b_1 89-90°, d_{20} 0.9561, n_D^{20} 1.5170. Similarly was prepd. 56% $[HB(SPr)_2]_2$, b_4 93-5°, 0.9809, 1.5265. Reaction of 0.07 mole B_2H_6 and 0.14 mole BuSH, run as above, followed by a passage of propylene 2 hrs. gave a range of products as follows: 7.9% Pr_3B, 40% Pr_2BSPr (I), b_2 64-70°, and 24% $[HB(SBu)_2]_2$. Passage of B_2H_6 2 hrs. into 10.1 g. I in Et_2O, followed by standing overnight and passage of propylene 2 hrs. as above, gave the same 3 products as above. Heating I with BuSH at 60-160° over 4 hrs. gave H_2 and 70% $B(SBu)_3$, b_1 150-2°, 0.9684, 1.5205. Similarly was prepd. 78% $B(SPr)_3$, b_4 133-5.5°, 0.9952, 1.5312. Mixing 16.? g. I and 4.8 g. $EtNH_2$ and keeping the mixt. 1 hr. gave after evacuation at 30-100° and distn. in vacuo, 77% N-triethylborazole, b_{20} 66-8°. Similarly $BuNH_2$ gave 66% N-tributylborazole, $b_{0.25}$ 78-80°, 0.8426, 1.4515.

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Organoboron compounds. XLV. Reaction of butyl esters of boric and organoboron acids with aromatic amines.

B. M. Mikhailov and P. M. Aronovich (Inst. Org. Chem., Acad. Sci., Moscow). Zhur. Obshchei Khim. 29, 3124-9 (1959). cf. Doklady Akad.Nauk SSSR 127, 571(1959).

Esters of B acids react at reflux with aromatic amines yielding the corresponding amino derivs. in reversible reactions. Kinetic curves for formation of typical products are shown. Completion of the reaction can be attained only if the resulting ROH is removed during the reaction. Slow distn. of BuOH from 0.1 mole $B(OBu)_3$, $PhB(OBu)_2$ or Ph_2BOBu and arom. amine (0.2-0.4 mole) at 210-250° gave the following amino derivs.: 50% $B(NHC_6H_4Me\text{-}p)_3$, m. 157-60°; 85% $PhB(NHPh)_2$, m. 84-6°; 67% $PhB(NHC_6H_4Me\text{-}p)_2$, m. 85-7°; 73% Ph_2BNHPh, b_1 202-6°, m. 56-8°; 44% $PrB(NHPh)_2$, b_1 162-3°, n_D^{25} 1.5837; $BuB(NHPh)_2$, 32%, b_1 169-71°, 1.5750; 38% Bu_2BNHPh, b_7 136-7°, 1.4995. Reaction of $PhB(O\text{-}CH_2CHMe_2)_2$ and 3 moles $p\text{-}MeC_6H_4NH_2$ was carried out as above and the residue, freed in vacuo of low b. materials was heated 1 hr. at 195° in vacuo yielding $p\text{-}MeC_6H_4NH_2$ and 42.5% B-triphenyl-N-tri-p-tolylborazole, m. 325-7°. Reaction of $PhB(NHPh)_2$ with iso-BuOH 3 hrs. at reflux gave 97% $PhNH_2$ and 73.5% $(iso\text{-}BuO)_2BPh$. $NaNH_2$ in liq. NH_3 treated with $(iso\text{-}BuO)_2BPh$ at -60° gave a grey $C_{14}H_{25}O_2NBNa$, possibly $(iso\text{-}BuO)_2B(NH_2)Ph$.Na salt.

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Organoboron compounds. XLVI. Dialkylboronic acids and their derivatives. B. M. Mikhailov and T. A. Shchegoleva (Inst. Org. Chem., Acad. Sci., Moscow). Zhur. Obshchei Khim. 29, 3130-5 (1959). cf. preced. abstr. All reactions described below were run under N atm. To EtLi soln. prepd. from 9.7 g. Li and 82 g. EtBr in Et_2O there was added in 1.5 hrs. 96.7 g. $BuB(OBu)_2$ at -25° to -70°; on the following day dry HCl was introduced and the pptd. inorg. salts were sepd.; the filtrate was concd. and ~~treatedwith~~ refiltered, after which it was distd., yielding 50% EtBuBOBu, b_7 65-7°, d_{20} 0.7866, n_D^{20} 1.4130. Similarly EtLi and $PrB(OBu)_2$ gave 31% EtPrBOBu, b_{40} 82-4°, 0.7748, 1.4090. PrMgBr and $PrB(OBu)_2$ similarly gave 45% Pr_2BOBu, b_{15} 76-6.5°, ~~Ame~~ 0.7777, 1.4133. Shaking 4.1 g. $Bu_2BOCH_2CH_2OBBu_2$ with 10 ml. 10% NaOH, followed by acidification with HCl and extn. with isopentane gave 92% Bu_2BOH, d_{20} 0.8105, which is very readily attacked by air. Similar treatment of Bu_2BOBu yielded a soln. of $(Bu_2B(OH)_2)Na$ (OBu) in H_2O, which on acidification gave Bu_2BOBu. If the reaction mixt. is directly evapd., there is isolated a colorless crystalline $(Bu_2B(OH)_2)Na$. Similarly PrBuBOBu and 10% NaOH gave on acidification 62% PrBuBOH, d_{20} 0.7986. Soln. of 8.6 g. Pr_2BOBu in 20 ml. 10% NaOH was freed of BuOH and H_2O in vacuo and the residue was taken up in H_2O and acidified yielding an org. layer which was extd. with Et_2O, evapd. and dehydrated by refluxing with C_6H_6; the residue gave 2.1 g. $(Pr_2B)_2O$, b_{10} 91.5-2°, 0.7743, 1.4170. This with 10% NaOH followed by dil. HCl gave 77% Pr_2BOH, d_{20} 0.7932, 1.4108, a liquid which is almost insol. in H_2O.

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Organoboron compounds. LI. Synthesis of alkylborodifluorides from trialkylboron and boron trifluoride etherate.

B. M. Mikhailov and T. A. Shchegoleva (Inst. Org. Chem., Acad. Sci., Moscow)

Zhur. Obshchei Khim. 29, 3443-5 (1959). cf. Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk 1959, 1869.

All reactions were run under N_2. To 58.6 g. iso-Am_3B heated to 200-10° was added over 6.5 hrs. 70.5 g. $BF_3.Et_2O$ and the distillate was fractionated yielding 77% iso-$BuBF_2$, b. 58°, d_{20} 0.9567. Similarly was prepd. 85% n-$C_6H_{13}BF_2$, b. 89-90°, Use of Bu_3B gave a soln. of $BuBF_2$ in Et_2O, b.39-40°, contg. a comparable amt. of $BuBF_2$ to the above runs. iso-$AmBF_2$ and MeOH form a complex iso-$AmBF_2$.2MeOH, b_{30} 34-7°, d_{20} 0.9473, n_D^{20} 1.3825. Also prepd. were: iso-$AmBF_2$.2BuOH, b_{10} 43-7°, 0.8891, 1.4050; $C_6H_{13}BF_3$.2BuOH, b_9 47-50°, 0.8901,-. $C_6H_{13}BF_2$ and $EtNH_2$ in Et_2O gave 75% $C_6H_{13}BF_2.EtNH_2$, m. 112-4°. Similarly was prepd. $BuBF_2$.iso-$BuNH_2$, m. 44-50°.

fuel development

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Organoboron compounds. 56. Synthesis of borontrialkyls from metaborates and their transformation into esters of dialkylboronic acids.

B. M. Mikhailov and V. A. Vaver (N.D.Zelinskii Inst. Org. Chem., Moscow). Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk 1960, 852-6. cf. Doklady Akad.Nauk SSSR 131, 843 (1960).

Esters of metaboric acid react, under N_2, with RMgX yielding R_3B. These are converted into R_2BOR' on being heated with R'OH. Thus, BuMgBr from 18.3 g. Mg in Et_2O treated rapidly without cooling with 22.5 g. $(iso\text{-}BuOBO)_3$ and refluxed 2 hrs. gave after treatment with 7% HCl , followed by washing with O_2-free H_2O, 78% iso-Bu_3B. Similarly iso-AmMgCl and $(iso\text{-}BuOBO)_3$ gave 75.1% iso-Am_3B, and $(C_6H_{11}OBO)_3$ and iso-PrMgCl gave 66.8% iso-Pr_3B. Heating 8.6 g. iso-Pr_3B with 8 g. sec-octyl alc. to 130°, finally to 180°, over 1.5 hrs. gave MeCH:CH_2, H_2 and C_2H_6 as gaseous products and 74.2% sec-octyl diisopropylboronate, b_{18} 119-20°, n_D^{20} 1.4202, d_{20} 0.7833. Similarly $C_6H_{11}OH$ gave the same gaseous products and 83.5% $C_6H_{11}OB(CHMe_2)_2$, b_8 83-3.5°, 1.4372, 0.8314. Bu_3B and iso-AmOH gave H_2, C_4H_{10}, C_4H_8 and 83.6% iso-$AmOBBu_2$, b_{15} 114.5-5.5°, 1.4240, 0.7907. PhOH and iso-Am_3B gave mixed isopentane and isoamylene, along with 75.1% ~~R~~ iso-Am_2BOPh, b_3 121-3.5°, 1.4712, 0.8697. The operations may be combined; thus, 0.5 mole RMgX treated over 10-15 min. with 0.055 mole (possibly an error-G.M.K.) $(iso\text{-}BuOBO)_3$ in 1:1 C_6H_6 soln., then refluxed 2 hrs., treated with 225 ml. 7% HCl, the org. layer sepd. and concd., then heated 2 hrs. with desired HO compd., gave the following esters: 85.4% $C_6H_{11}OBBu_2$, b_9 120.5-1°, 1.4460, 0.8416; 87.2% Bu_2BOCH_2Ph, b_8 141.5-2°, 1.4793, 0.8871; 87.7% $C_6H_{11}OB(CH_2CHMe_2)_2$, b_7 104-5°, 1.4421, 0.8331; 86.6% $C_6H_{11}OB(CH_2CH_2CHMe_2)_2$, b_9 133.5-4°, 1.4472, 0.8392; and 92.3% iso-Am_2BOCH_2Ph, $b_{4.5}$ 141.5-2°, 1.4760, 0.8790.

15 Amines with gangliolytic activity. I. Amines of the cyclopentane and cyclohexane series.

N. K. Kochetkov, A. Ya. Khorlin, K. I. Lopatina and L. A. Vorotnikova (Pharmacol. Chemotherap. Inst., Acad. Med. Sci.). Zhur. Obshchei Khim. 29, 3613-6 (1959). cf. Stein et al. JACS 78, 1514 (1956).

To 0.1 mole ROH (tert. alc. from cyclopentanone or cyclohexanone and various Grignard reagnets) and 0.2 mole MeCN was added with cooling 0.2 mole 98% H_2SO_4 at below 40°; after 1 day at room temp. the mixt. was poured on ice and neutralized with NH_4OH yielding the following $(CH_2)_n$-CRNHCOR' (n, R, R' shown resp.): 4, Me, Me, 57%, m. 98-9°; 4, Et, Me, 36%, m. 86-7°; 4, Pr, Me, 59%, m. 111-1.5°; 4, Bu, Me, 25%, m. 89-90°; 5, Me, Me, 35%, m. 83-4°; 5, Et, Me, m. 71-2°; 5, Pr, Me, 72%, m. 69-70°./ To 0.2 mole KCN in 0.1 mole ROH (note above) in 20 ml. $EtCO_2H$ was added at below 10° 0.3 mole 98% H_2SO_4 yielding after 1 day at room temp. and an aq. treatment as above the following 1-alkyl-1-formamidocycloalkanes (notation as above): 4, Et, H, 82%, b_5 128-30°; 5, Et, H, 65%, b_3 130-2°. The amides reduced with $LiAlH_4$ in refluxing Et_2O to $(CH_2)_nCRNHCH_2R'.HX$ (n, R, R', X shown resp.)] 4, Me, Me, Cl, 65%, m. 184-5°; 4, Et, Me, Cl, 61%, m. 193-4°; 4, Pr, Me, Cl, 52%, m. 154-5°; 4, Bu, Me, Cl, 60%, m. 147-8°; 5, Me, Me, Cl, 59%, m. 203-4°; 5, Et, Me, Cl, 60%, m. 193-4°; 5, Pr, Me, Cl, 58%, m. 191-2°; 4, Et, H, C_2O_4H, 60%, m. 163-4°; 5, Et, H, C_2O_4H, 57%, m. 173-4°. The products showed some ganglioblocking activity the most active being the amine 4, Et, Me; the cyclohexane derivs. are less active. Hence the pertinence of the bicyclic isocamphane structure to ganglioblocking activity is disproved. A rigid alicyclic ring appears to be important, however.

organic nitrogen compounds
affecting nervous system - Way out of
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Amines with gangliolytic activity. II. Aliphatic amines with tertiary radicals.

N. K. Kochetkov, A. Ya. Khorlin, L. A. Vorotnikova and K. I. Lopatina (Pharmacol. Chemotherap. Inst., Acad. Med. Sci.). Zhur. Obshchei Khim. 29, 3616-9 (1959).

A new group of active gangliolytic substances was discovered, of which the most active was ethyl-(3-ethyl-2-pentyl)-amine. The compds. as a group produced considerable ganglioblocking activity at 2-4 mg/kg on unspecified test animals. Treatment of appropriate alcs. with 2 moles MeCN followed by 2 moles 98% H_2SO_4 2 days at room temp. gave after neutralization with NH_4OH, the following RNHCOR' (R and R' shown resp.): Me_3C, Me, 50%, m. 97-8°; Me_2EtC, Me, 51%, m. 78-80°; $MeEt_2C$, Me, 50%, m. 80-2°; Et_3C, Me, 55.5%, m. 86-7°; Me_3CCMe_2, Me, 78.9%, m. 109-10°; $Me_3CCMeEt$, Me, 52%, m. 107-9°; Me_2CPr, Me, 30%, m. 57-8°; Me_2CHCMe_2, Me, 30%, m. 62-4°; MeEtPrC, Me, 32%, b_5 104-6°; Me_2BuC, Me, 93%, m. 65-7°; Me_3CCMe_2, H, 32%, m. 129-30°; Et_3C, H, 53%, m. 98-100°. The formamides listed above were prepd. similarly from KCN and appropriate alc. in AcOH. Reduction of the amides with $LiAlH_4$ in Et_2O gave $RNHCH_2R'.HCl$ (R and R' shown resp.): Me_3C, Me, 60%, m. 204-5°; Me_2EtC, Me, 60%, m. 151-3°; $MeEt_2C$, Me, 55%, m. 160-2°; Et_3C, Me, 83.8%, m. 178°; Me_3CCMe_2, Me, 80%, m. 256-8°; $Me_3CCMeEt$, Me, 80%, m. 209-11°; Me_2PrC, Me, 50%, m. 130°; Me_2CHCMe_2, Me, 53%, m. 174-6°; MeEtPrC, Me, 63.3%, m. 153-6°; Me_2BuC, Me, 66%, m. 153-5°; Me_3CCMe_2, H, 63%, m. 232-2.5°; Et_3C, H, 50%, m. 171-2°.

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Approved For Release 2009/08/25 : CIA-RDP80T00246A011800280001-0